

AMENDED SPECIFICATION

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PATENT SPECIFICATION

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(54) A PROCESS FOR THE PRODUCTION OF ISOCYANATES

(71) We, **FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT**, of 509, Leverkusen, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of isocyanates.

4,4'-Diisocyanato diphenylmethane, a starting material for the production of polyurethane elastomers and coatings, is commercially produced from 4,4'-diamino diphenylmethane by reaction with phosgene in inert solvents, usually in chlorobenzene. The diamine is obtained by condensation in aqueous hydrochloric acid solution of aniline and formaldehyde from which a polyamine mixture containing the diamine as the main constituent is formed. The compounds with more than two nuclei can be separated off at the amine stage. Unfortunately, distillation of the polyamine mixture is complicated by the high boiling point and the solidification point of 4,4'-diamino diphenylmethane (92° C). Thus, polyamines left in the residue are solid at room temperature and are difficult to handle or the distillation involves considerable losses if diamines are left in the amine residue in order to improve the flow properties.

It is much simpler to react the polyamine mixture prepared from aniline and formaldehyde as a whole with phosgene to form a polyisocyanate mixture and then to distil off 4,4'-diisocyanato diphenylmethane from this polyisocyanate mixture. The disadvantage of this process is that the unwanted higher-

functional polyamines are also reacted with phosgene and are lost either as isocyanates or as by-products which are derived from the isocyanates, for example as carbodiimides and carbodilimide-isocyanate adducts. A 4,4'-diisocyanato diphenylmethane which is at least 98% pure can not be obtained in this way because diamines with an NH₂ in the ortho-position, based on the methylene group in the diphenylmethane structure, are also formed during the aniline-formaldehyde condensation, and because the 2,2'- and 2,4'-diisocyanato diphenylmethane distil over together with the 4,4'-isomer during the distillation of a mixture.

It is an object of the present invention to provide a method of obtaining at least 98% by weight pure 4,4'-diisocyanato diphenylmethane from the phosgenation product of a polyamine mixture of this kind which has been obtained by condensing aniline and formaldehyde and also provides valuable starting materials for the production of polyurethanes which are also simultaneously obtained from the phosgenation products of the higher-functional polyamines.

The invention provides a process for the production both of (II) at least 98% by weight pure 4,4'-diphenylmethane diisocyanate and a polyphenylpolymethylene - polyisocyanate mixture (III) from a polyisocyanate mixture (I) which has been obtained by condensation of aniline and formaldehyde, followed by phosgenation of the condensation product, wherein the polyisocyanate mixture (I) is separated by fractional distillation into a fraction A which consists mainly of isomeric diphenylmethane diisocyanates, and a fraction B which, in addition to isomeric diphenyl

methane diisocyanates, consists of polyisocyanates containing more than two aromatic nuclei, and in which fraction A is then separated by fractional distillation into a fraction C consisting of 2,2'-, 2,4'- and 4,4'-diphenylmethane diisocyanates, and a fraction D at least 98% by weight of which consists of 4,4'-diphenylmethane diisocyanate and into a residue E comprising material formed as a result of high temperature polymerisation and in which fraction C is mixed with at least part of fraction B to produce a mixture having a K-value (as herein defined) of greater than 1.3 which mixture is product (III); the product (II) being fraction D.

If desired fraction C may be mixed not only with at least part of fraction B but also with residue E to give product (III).

Various components in the polyisocyanate mixture (I) used as starting material in the process according to the invention can be quantitatively detected by gas chromatography. These components include *inter alia* the dinuclear isomers 2,4'-diphenylmethane diisocyanate and 4,4'-diphenylmethane diisocyanate and the trinuclear isomers 1 - (4-isocyanato phenylmethyl) - 3 - (2 - isocyanato phenylmethyl) - 4 - isocyanato benzene (3 K I) and 1,3 - di - (4 - isocyanato phenylmethyl) - 4 - isocyanato benzene (3 K II). In order to clarify the description, the ratio between the gas-chromatographically determined concentrations of the dinuclear 2,4'- and 4,4'-isomers will be referred to simply as *a*, and the ratio between the concentrations of the trivalent isomers 3 K I:3 K II referred to simply as *b*.

In a polyisocyanate mixture of the kind which is obtained by the condensation of aniline and formaldehyde, followed by phosgenation of the condensation product, the ratio of ortho- and para-compounds and the ratio of dinuclear to higher-nuclear compounds vary within wide limits depending upon the concentration of the starting materials, aniline, formaldehyde and acid catalyst, upon the temperature and upon the pH value at which condensation is carried out. However, the ratio between the ratios *a* and *b* defined above remains equal to a factor K, largely independent of the above reaction conditions. The value for K is between 0.4 and 1.2. In contrast, the ratio is greater by at least 0.1 in the polyisocyanate mixtures (III) prepared by the process according to the invention which have a higher concentration of 2,4'-isomers than the undistilled starting material. The result of this is that, in the polyisocyanate mixtures (III) prepared by the process according to the invention, the factor K is always greater than 1.3 and usually lies between 1.4 and 100.

Apart from the polyisocyanate mixture thus defined, it is also possible by the process according to the invention to produce at least

98% by weight pure 4,4'-diphenylmethane diisocyanate (II).

The starting material is a polyamine mixture which is prepared from aniline and formaldehyde which is then reacted with phosgene in an inert solvent, for example in chlorobenzene, to give the polyisocyanate mixture (I). Accordingly, there is no need to prepare two different condensation products from aniline and formaldehyde, one for the production of 4,4'-diisocyanato diphenylmethane and the other for the production of polyisocyanate mixtures which are liquid at room temperature and have diphenylmethane structures.

The composition of the starting material, a mixture of polyisocyanates of the diphenylmethane series, is not critical for the practical application of the process. Polyisocyanate mixtures with a diisocyanate content of from 40 to 80% by weight and a 2,4'-isomer content in the diisocyanate component of from 1 to 40% by weight, are readily obtained on a large scale, although it is preferred to use polyisocyanate mixtures containing from 50 to 70% by weight diisocyanate and with from 4 to 8% by weight of 2,4'-isomers in the diisocyanate component. The preparation of polyamine mixtures which with phosgene yield polyisocyanate mixtures such as these is advantageous in regard to volume-time yield, acid, alkali and energy consumption.

As in the subsequent distillations, the first stage of the process in which a fraction A, namely a mixture of 2,2'-, 2,4'- and 4,4'-diisocyanate diphenylmethane, is separated from the starting material by distillation, has to be carried out in a manner which prevents the isocyanate groups from being degraded by heat. Apparatus which is suitable for this purpose includes falling-film evaporators operated continuously under a vacuum below 15 Torr, through which some of the material to be evaporated is repeatedly circulated by means of rotary pumps. Up to 70% by weight of diisocyanate can be distilled off, depending upon the diisocyanate content of the starting material. The operation can be controlled by monitoring the viscosity of the concentrate from which diisocyanate has been removed, namely the fraction B. The viscosity of the concentrate is between 200 and 10,000 cP/25° C, depending upon the quantity of diisocyanate mixture distilled off. The concentrate B from which diisocyanate has been removed does not show such a marked tendency as a polyisocyanate mixture enriched with 4,4'-diisocyanate diphenylmethane to form sediment containing uretdione groups at temperatures in a range from 40 to 150° C.

The diisocyanate mixture A obtained from the starting product is fractionated in a multiple stage column under a reflux of from 0.5:1 to 20:1, the 2,2'- and 2,4'-isomers preferentially distilling over with the fraction

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C (first runnings), leaving behind a fraction D with the 4,4'-isomer. A vacuum at the head of the column of from 0.2 to 4 Torr is required for this distillation. Even when using columns which have limited pressure losses, for example columns with packings of profiled steel plate or helical springs or with wire-gauze packings, and evaporators with little or no pressure losses are used, a boiling point above 150° C (at which 4,4'-diisocyanato diphenylmethane decomposes to form carbodiimides) is adjusted at the sump of the column. After fractionation, the sump product E always contains polymer which is separated off from pure 4,4'-diisocyanato diphenylmethane by another distillation using a falling-film evaporator. The sump product E, usually amounting to less than 5% by weight of the diisocyanate used, remains liquid with a monomeric diisocyanate content of more than 50% by weight. It is suitable for the production of polyurethane plastics, if desired in admixture with first runnings C and concentrate B.

Fractionation of the diisocyanate mixture A can be combined with a treatment with iron chloride which is used to convert chlorine-containing impurities into a non-volatile form. The fractionation column may also be preceded by a distillation vessel operated in a vacuum of from 3 to 20 Torr. The object of the distillation is to remove traces of solvents which would interfere with the higher vacuum which is used in the fractionation column. The distillation vessel also acts as a container in which iron chloride is brought into contact with the chlorine-containing impurities at temperatures above 150° C.

Several fractionation columns can be arranged in series, in which case the following column is filled with head product from the preceding column, and the sump product mixed with the material running into the preceding column. This arrangement enables each column to be operated with a lower pressure loss, i.e. at a lower sump temperature, because the number of necessary separation units is distributed over several columns. It also enables polymer formation from the isocyanate to be reduced.

It is best to operate all this apparatus on a continuous cycle in order to keep the first runnings, the pure distillate and the polymer uniform in quality.

With fraction C, it is possible under favourable conditions to separate more than 90% by weight of the 2,2'- and 2,4'-isomers in a single distillation stage, depending upon how the columns are operated and arranged. However, if an increase in concentration which can be obtained in a column with more than 50 theoretical plates or a reflux ratio of greater than 10:1 is obtained, there is an increase in the residence time and in the sump temperature which is usually governed by the differ-

tial pressure in the column and hence in polymer formation and in the losses of 4,4'-diisocyanato diphenylmethane. Hence distillation in columns arranged one after the other is preferred. It is possible by repeated fractionation to obtain the 2,2'- and 2,4'-isomers having a purity of more than 95% by weight.

The fraction D has a 4,4'-diisocyanato diphenylmethane content of at least 98% by weight and can be processed so that it has a 4,4'-diisocyanato diphenyl methane content of more than 99% by weight, again depending upon the method of operation. A product as pure as this cannot be obtained directly by condensing aniline and formaldehyde, phosgenating the product of condensation, distilling off the product of condensation and distilling off the diisocyanate.

In order to mix concentrate B with the first runnings C, it is possible to collect the concentrate B immediately after it has been prepared in a vessel containing first runnings C from the separation of the isomers or continuously to mix it with the first runnings C accumulating from separation of the isomers and to obtain the required setting in this way. It is also possible in the process according to the invention to mix only part of the concentrate B with the first runnings C and to obtain a product which contains more diisocyanate and which is more free-flowing than the polyisocyanate mixture used for distillation.

The 2,2'- and 2,4'-diisocyanato diphenylmethane introduced in the first runnings C provides the mixture (III) with properties which are advantageous in many respects. Since 4,4'-diisocyanato diphenylmethane is usually the predominating constituent of the starting material, this compound initially crystallises on cooling. The exchange of 4,4'- for 2,2'- and 2,4'-isomers improves the resistance of the mixture to low temperatures.

Another advantage of the process according to the invention is that it enables the isomer content of the end products to be adjusted and kept very uniformly to the required level. For example, the amount of 2,4'- in 4,4'-diisocyanato diphenylmethane can be kept under 1% ± 0.2%.

In aromatic polyisocyanates, NCO groups in the ortho-position react more slowly with hydroxyl compounds than NCO groups in the para-position. Accordingly, the polyisocyanate mixtures (III) according to the invention enriched with 2,2'- and 2,4'-isomers are eminently suitable for the production of polyurethane lacquers whose pot-life is longer than that of lacquers which have a higher 4,4'-isomer content, for the above reason. Since the viscosity of the polyisocyanate mixtures (III) according to the invention can be adjusted by the quantity of 2,2'- and 4,4'-isomers added, the mixtures (III) according to the invention represent interesting starting materials for the production of foams. For example,

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they can be used to produce foams in moulds and by using the flow properties of the material these can readily be adapted to the moulds. The polyisocyanate mixtures (III) according to the invention are also suitable for the production of core sand binders, sealing compositions, coatings and other materials.

4,4'-Diisocyanato diphenylmethane of low isomer content (II) according to the invention is an excellent starting material for the production of elastic fibres, homogeneous and microporous coatings and elastomers and the invention extends to such materials.

Polyphenyl - polymethylene - polyisocyanato mixtures (III) are excellent starting materials for polyurethane (urea) lacquers, coatings, films, foams, foundry core binders and sealing compositions, and the invention extends to such materials.

The following Examples illustrate the invention (in these examples, percentage contents are by weight, unless otherwise specified):—

Example 1.

A polyisocyanate mixture (viscosity 100 cP/25° C) containing 3.5% of 2,4'-diisocyanato diphenylmethane,

59.4% of 4,4' - diisocyanato diphenylmethane,

1.2% of 1 - (4 - isocyanato phenylmethyl) - 3 - (2 - isocyanato phenylmethyl) - 4 - isocyanato benzene,

20.6% of 1,3 - di - (4 - isocyanato phenylmethyl) - 4 - isocyanato benzene, and

8.6% of tetranuclear isocyanates,

is separated in a falling-film evaporator into a fraction A containing 0.1% of 2,2' - diisocyanato diphenylmethane,

5.1% of 2,4' - diisocyanato diphenylmethane, and

94.7% of 4,4' - diisocyanato diphenylmethane,

and a polyisocyanate mixture (fraction B) with a viscosity of 800 cP/25° C. The diisocyanate mixture to which 200 ppm of ferric chloride are added passes continuously through a distillation column or gas-separation column, a fractionation column (Montz/Kloss system) with an exchange height of 17 metres and a falling-film evaporator of the Sambay type.

The object of gas separation carried out under a vacuum of 8 Torr and at a temperature of 200° C is to remove small quantities of chlorobenzene remaining from the phosgenation process. In the column, an isomer mixture containing 0.4% of 2,2'-, 22.0% of 2,4'- and 77.6% of 4,4'-diisocyanato di-

phenylmethane is run off under a vacuum of 3 Torr at the head of the column and at a sump temperature of 210° C (reflux ratio 4:1).

For evaporation, a stream of the sump product is pumped through a vertically arranged steam-heated tubular heat exchanger by means of a rotary pump arranged at the bottom of the column. A second stream from the same pump is delivered to a similarly steam-heated falling-film evaporator in which it is separated into 4,4' - diphenylmethane diisocyanate (fraction D) and a sump product (E). The distillate is converted into a flaky product by means of a cooling roller. Analysis by gas chromatography shows that this product (II) contains 0.6% of 2,4'-diisocyanato diphenylmethane, solidified at 39.1° C and has a residual chlorine content of less than 20 ppm.

The sump product E which is viscous at room temperature is collected in a container from which it is added to the polyisocyanate mixture B (viscosity 800 cP/25° C).

Addition of 27 parts of fraction C from the fractionation column to 73 parts of the aforementioned polyisocyanate mixture B combined with the sump product E forms the end product with the following analytical data:

Viscosity 205 cP/25° C,

30.6% of NCO

0.15% of hydrolysable chlorine,

0.39% of total chlorine,

74 ppm of iron,

7.4% of 2,4' - diisocyanato diphenylmethane,

53.2% of 4,4' - diisocyanato diphenylmethane,

1.1% of 1 - (4 - isocyanato phenylmethyl) - 3 - (2 - isocyanato phenylmethyl) - 4 - isocyanato benzene,

22.9% of 1,3 - di - (4 - isocyanato phenylmethyl) - 4 - (isocyanato benzene), and

6.5% of tetranuclear isocyanates.

This isocyanate is foamed with a polyol mixture consisting of 40% of a polyester with an OH number of 380, 30% of a polyether with an OH number of 380 and 30% of a polyether with an OH number of 550.

These polyethers were obtained by reacting a trifunctional alcohol with propylene oxide. The polyol mixture also contains 3% by weight of a 50% aqueous solution of the sodium salt of sulphonated ricinoleic acid, 1.2% by weight of a commercial polyether siloxane and 1% by weight of a tertiary amine. 100 Parts of the mixture are reacted with 130 parts by weight of the above isocyanate following the addition of 40 parts by weight of fluorotrichloromethane in an HK spraying machine, model 100 (System Bayer).

The following reaction times are observed:

Starting time	Setting time	Expanding time
8	70	120 seconds

- 5 A closed-cell hard foam with a unit weight of 23 kg/m³ is obtained. This foam remains dimensionally stable after storage for 1 hour at -10° C.

Example 2.

- 10 This example compares the results obtained using polyisocyanate mixtures which have been prepared from a uniform polyisocyanate mixture obtained by phosgenation of a polyamine mixture obtained by aniline/formaldehyde condensation. By distilling off various quantities of diisocyanate, polyiso-

cyanate mixtures with reduced diisocyanate contents are obtained. Isocyanate mixtures of comparable viscosity are produced from these polyisocyanate mixtures of reduced diisocyanate content by mixing again with diisocyanate. The results are given in the table, in which:

X refers to diisocyanate as obtained from the distillation without accumulation of the 2,4'-isomer, and

Y refers to diisocyanate as obtained by fractional distillation of X as the head product with enriched 2,4'-isomers.

Z refers to an isocyanate mixture which was adjusted to the desired viscosity simply by distilling off diisocyanate and to which no diisocyanate has been added.

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Isocyanate Mixture No.:	1	2	3	4	5	6	7	8
Viscosity cps/250 after distilling off diisocyanate (= stock)	435	1250	1250	200	435	435	1250	1250
Mixed with diisocyanate	Y*	Y*	X	Z	X	Y*	X	Y**
Ratio, Stock : diisocyanate	74:26	63:37	63:37	100:0	85:15	85:15	73:27	73:27
Viscosity of the mixture cps: 25°C	124	118	115	200	180	185	210	188
2,4'-diisocyanate % by weight	11.7	15.2	2.2	1.4	1.3	6.7	2.3	12.4
4,4'-diisocyanate % by weight	44.4	38.9	50.3	45.2	50.2	42.3	46.2	35.8
3-Nuclear isocyanate I % by weight (3 K I)	1.0	0.9	0.9	1.4	1.2	1.2	1.1	1.2
3-Nuclear isocyanate II % by weight (3 K II)	18.2	19.2	19.3	25.7	22.8	22.8	21.8	22.1

* Content 40% 2,4'-isomers by weight

** Content 50% 2,4'-isomers by weight

Ratio:

2,4'-: 4,4'- (- a)	0.263	0.391	0.044	0.031	0.026	0.158	0.050	0.347
3 n I : 3 n II (- h)	0.055	0.047	0.047	0.055	0.053	0.053	0.050	0.054
a : h	4.8	8.3	0.9	0.6	0.5	3.0	1.0	6.4

Rigid-foam test specimens are produced from the isocyanate mixtures with a polyol component which contains activators, foam control agents and a blowing agent.		dimethylethylamino - piperazine, 0.4 part by weight of pentamethyl diethylene triamine, 100 parts by weight of the polyol component and 40 parts by weight of monofluorotrichloromethane		25
5	Polyol component: 40 parts by weight of polyester prepared from phthalic anhydride, adipic acid, oleic acid, and trimethylol propane of OH number 370 and viscosity 1400 cps/75° C,	are foamed on a high pressure foaming machine of the type HK 100 at 20° C with 130 parts by weight of isocyanate mixture.		30
10	30 parts by weight of polyether prepared from trimethylol propane and propylene oxide of OH number 360 and viscosity 650 cps/25° C,	In a first experiment "prism test", the foam mixture flows into a prismatic mould with a base area 25×25×25 cm edge length.		35
15	1.2 parts by weight of polysiloxane polyalkyl ether, 3 parts by weight of a 50% aqueous solution of sodium castor oil sulphate,	450±30 g of foam are allowed to rise in this mould, the velocity of flow and the expansion height being measured. In a second experiment "board test", 600±10 g of foam mixture are charged into a mould having dimensions 200×20×5 cm and heated to 45° C; the expansion properties are tested		40
20	0.6 part by weight of N - methyl - N,N'-			

Result with isocyanate Mixture:		1	2	3	4	5	6	7	8
Prism test:									
Weight of the foam specimen (g)		920	920	950					
Maximum rise (mm)		1690	1730	1685					
Foam height reached after (sec)		80	80	90					
Board test:									
Weight of the foam specimen (g)		600	600	600	600	600	600	600	600
Rise (%) (Maximum 2 m)		99.5	99	96	96	96	99.5	96	99.5

The samples with increased content of 2,4'-diisocyanate showed improved flow properties.

Example 3.

This comparison example refers to isocyanate mixtures Nos. 2 and 3 of the preceding example, which are processed after addition of 0.2% by weight each of isophthalyl chloride with a polyol component to give a coating composition.

Polyol component

1200 Parts by weight of a polyether com-

Titanium dioxide (rutile type)
Quartz powder (0.03 to 0.2 mm)

800 parts by weight
5300 parts by weight

This batch is homogenised with a mechanical agitator for twenty minutes and degasified in a vacuum unit at a pressure of 30 Torr for ten minutes. The product thus produced is the component I of a solvent-free coating composition.

For testing the pot-life, 100 parts by weight of the batch are removed and mixed with 23 g of polyisocyanate. A free-flowing mass is obtained which can be processed by casting and solidifies within 24 hours to a hard plastic. A comparison test shows that the pot-life with the isocyanate mixture No. 2 is seventy minutes. With the isocyanate mixture No. 3, however, the pot-life is only forty minutes.

WHAT WE CLAIM IS:—

1. A process for the production both of (II) at least 98% by weight pure 4,4'-diphenylmethane diisocyanate and (III) a polyphenyl-polymethylene-polyisocyanate mixture from a polyisocyanate mixture (I) which has been obtained by condensation of aniline and formaldehyde, followed by phosgenation of the condensation product, wherein the polyisocyanate mixture (I) is separated by fractional distillation into a fraction A which consists mainly of isomeric diphenylmethane diisocyanates, and a fraction B which, in addition to isomeric diphenylmethane diisocyanates, consists of polyisocyanates containing more than two aromatic nuclei, and in which fraction A is then separated by fractional distillation into a fraction C consisting of 2,2', 2,4'- and 4,4'-diphenylmethane diisocyanates, and a fraction D at least 98% by weight of which consists of 4,4'-diphenylmethane diisocyanate and into a residue E comprising material formed as a result of high temperature polymerisation and in which fraction C is mixed with at least part of fraction B to produce a mixture having a K-value (as herein

pound which has an OH content of 11.5% and a viscosity of 700 cps (25° C) produced by reacting propylene oxide with trimethylol propane are mixed with 2200 parts by weight of castor oil first pressing (OH content 4.8%), 500 parts by weight of sodium aluminium silicate of the zeolite type are dispersed in this mixture. The sodium aluminium silicate used has a water content of <2.5%. The following are used as further components of the mixture:

defined) of greater than 1.3 which mixture is product (III); the product (II) being fraction D.

2. A process as claimed in claim 1 in which the polyisocyanate mixture (I) used contains 40 to 80% by weight of diisocyanate which has a 2,4'-isomer content of 1 to 40% by weight.

3. A process as claimed in claim 2 in which the mixture (I) contains 50 to 70% diisocyanate by weight and 4 to 8% by weight of 2,4'-isomers.

4. A process as claimed in any of claims 1 to 3 in which up to 70% by weight of the diisocyanate is distilled off in fraction A.

5. A process as claimed in any of claims 1 to 4 in which fractionation of the diisocyanate mixture A is combined with a treatment with an iron salt to remove chlorine-containing impurities.

6. A process as claimed in any of claims 1 to 5 in which fraction C is mixed not only with at least part of fraction B but also with residue E to give product (III).

7. A process as claimed in claim 1 substantially as herein described with reference to any one of the Examples.

8. Product II which contains at least 98% by weight of 4,4'-diphenylmethane diisocyanate when produced by a process as claimed in any of claims 1 to 7.

9. A polyphenyl-polymethylene-polyisocyanate mixture (III) when prepared by a process as claimed in any of claims 1 to 7.

10. Polyurethane (urea) elastomers, fibres, films, foams and microporous sheets when produced using 4,4'-diisocyanato diphenylmethane as claimed in claim 8.

11. Polyurethane (urea) lacquers, coatings, films, foams, foundry core binders and sealing compositions when produced using a polyphenyl-polymethylene-polyisocyanate mixture (III) as claimed in claim 9.

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